Solution to problem set 11 (last one)

7.21 Mechanism given as A + B → P where k = $10^5 M^{-1}s^{-1}$ @ 27^oC.

a) If $[A]_0 = [B]_0$ = 0.10M @ 27^oC, calculate initial formation rate of P

$$\frac{dP}{dt} = k[A][B] = 10^5 M^{-1}s^{-1} \times (0.1M)(0.1M) = 10^3 Ms^{-1}$$

b) If $[A]_0 = 10^{-4}$M & $[B]_0 = 10^{-6}$M @ 27^oC, calculate initial formation rate of P

$$\frac{dP}{dt} = k[A][B] = 10^5 M^{-1}s^{-1} \times (10^{-4} M)(10^{-6} M) = 10^{-5} Ms^{-1}$$

c) If $[A]_0 = [B]_0$ = 0.10M @ 27^oC, how long would it take to form 0.050M product?

$$kt = \frac{1}{[A]} - \frac{1}{[A]_0} \Rightarrow 20 - 10 = 10^5 t \Rightarrow t = 10^{-4} s$$

d) At 127^oC, k increases by a factor of 10^3. Calculate E_a and ΔH* (I can't find the double dagger in MS Word, so I'll just use the asterisk) at 27^oC.

$$\ln\frac{k_2}{k_1} = \ln 10^3 = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \Rightarrow E_a = 8289K \times R = 8289K \times 0.008314 kJmol^{-1}K^{-1} = 68.9 kJmol^{-1}$$
$$\Delta H^* = E_a - RT = 68.9 kJmol^{-1} - (0.008314 kJmol^{-1}K^{-1})(300K) = 66.42 kJmol^{-1}$$

7.28 iso-allo isomerization

a) if iso/allo = 0.42 and $[allo]_0 = 0$, calculate $[allo]/[allo]_{eq}$.

Assuming 1 mole of iso (starting quantity not really important), let x = amount of allo formed. At equilibrium:

$$\frac{x^{eq}}{1 - x^{eq}} = 1.38 \Rightarrow x^{eq} = \frac{1.38}{2.18} = 0.580$$

At present:

$$\frac{x}{1-x} = 0.42 \Rightarrow x = \frac{0.42}{1.42} = 0.296 \Rightarrow\Rightarrow \frac{x}{x^{eq}} = \frac{[allo]}{[allo]^{eq}} = 0.510$$

b) if age = 38,600years, estimate the half-life of the isomerization process

$$\frac{[allo]}{[allo]^{eq}} = 0.51 = 1 - e^{-kt} = 1 - e^{-k(38600\,years)} \Rightarrow k = 1.848 \times 10^{-5} yr^{-1} \Rightarrow t_{1/2} = \frac{\ln 2}{k} = 37{,}500\,years$$

c) Calculate average T_{ground}. Current $T_{spring} = 28^oC$.

$$\ln\frac{k_2}{k_1} = \ln\frac{125000}{37500} = \ln 3.333 = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = -\frac{139.7}{0.008314}\left(\frac{1}{T_2} - \frac{1}{293K}\right) \Rightarrow T_2 = 299K$$

7.29 T-jump experiment

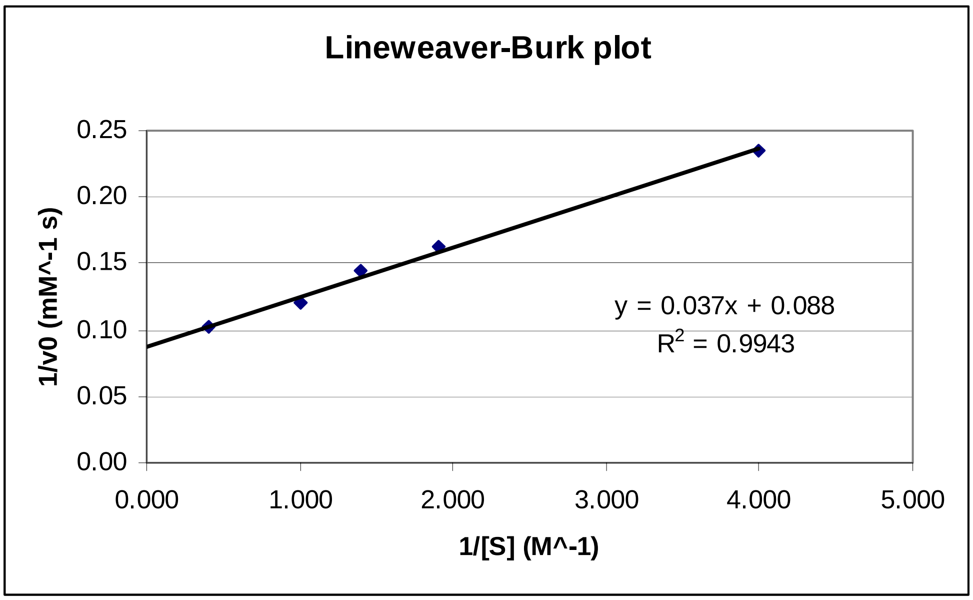
a) Calculate k_1 & k_{-1}

$$\tau^{-1} = k_1 + k_{-1} = (3\times10^{-3}\,s)^{-1} = 333.33s^{-1}$$
$$K = \frac{[B]^{eq}}{[A]^{eq}} = 10 = \frac{k_1}{k_{-1}} \therefore k_1 + k_{-1} = 10k_{-1} + k_{-1} = 11k_{-1} = 333.33s \Rightarrow k_{-1} = 30.3s^{-1} \;\&\; k_1 = 10k_{-1} = 303s^{-1}$$

b) Measured at T = 28°C.

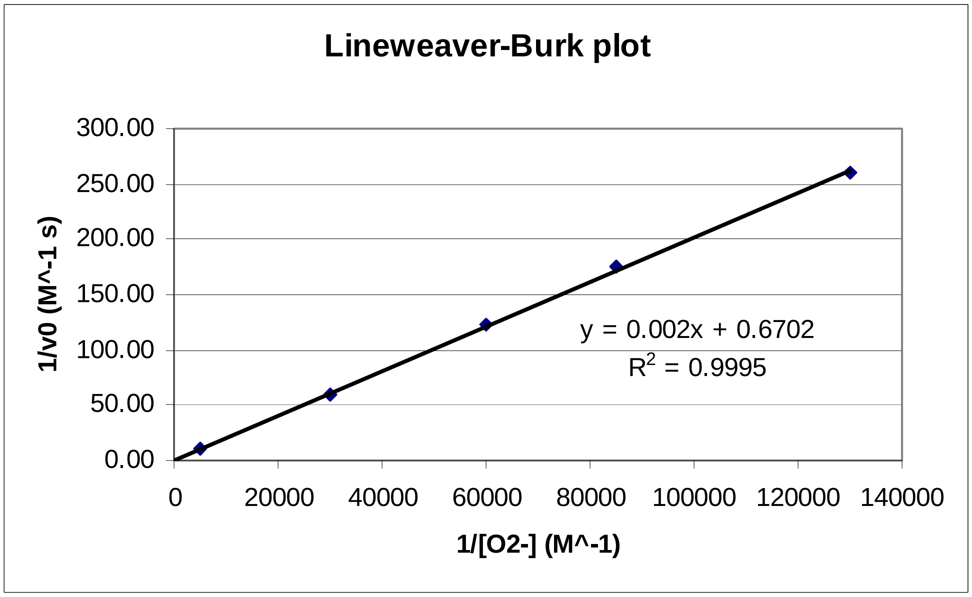
c) Doubling [tRNA] should have no effect on τ, k_1 & k_{-1}

8.1 Decarboxylation of β-keto acid. I used the inverse of the data points in the plot below. The y-intercept is 0.088 = $1/V_{max}$ therefore, V_{max} = 11.36mMs^{-1}. The slope is 0.037 = K_M/V_{max}, therefore, $K_M = (0.037)V_{max}$ = 0.42M.



8.15 enzyme SOD

a) Lineweaver-Burk plot



b) An extrapolation of the linear fit shows the data approaching the origin; this means that both $1/V_{max}$ and $1/K_m \rightarrow 0$

c) $k_2 >> (k_1 + k_{-1})$ implies that the complex ES dissociates to form E + P as soon as it is formed.

d) First order; because v_0 is directly proportional to $[O_2^-]$.

e) $V_0 = k[E]_0[O_2^-]$

$K[E]_0 = 5 \times 10^2 s^{-1}$ from slope of v_0 versus $[O_2^-]$ plot.

$$k = \frac{5\times10^2 s^{-1}}{4\times10^{-7} M} = 1.25\times10^9 M^{-1}s^{-1}$$

which is a value close to the diffusion limit.

f)

$$v_0 = k_1[E][O_2^-] + k_2[E^-][O_2^-] = [O_2^-](k_1[E] + 2k_1[E^-]) = k_1[O_2^-]([E] + 2[E^-])$$

where $([E] + 2[E^-])$ = constant x $[E]_0$ because the two terms in the velocity law must be identical.

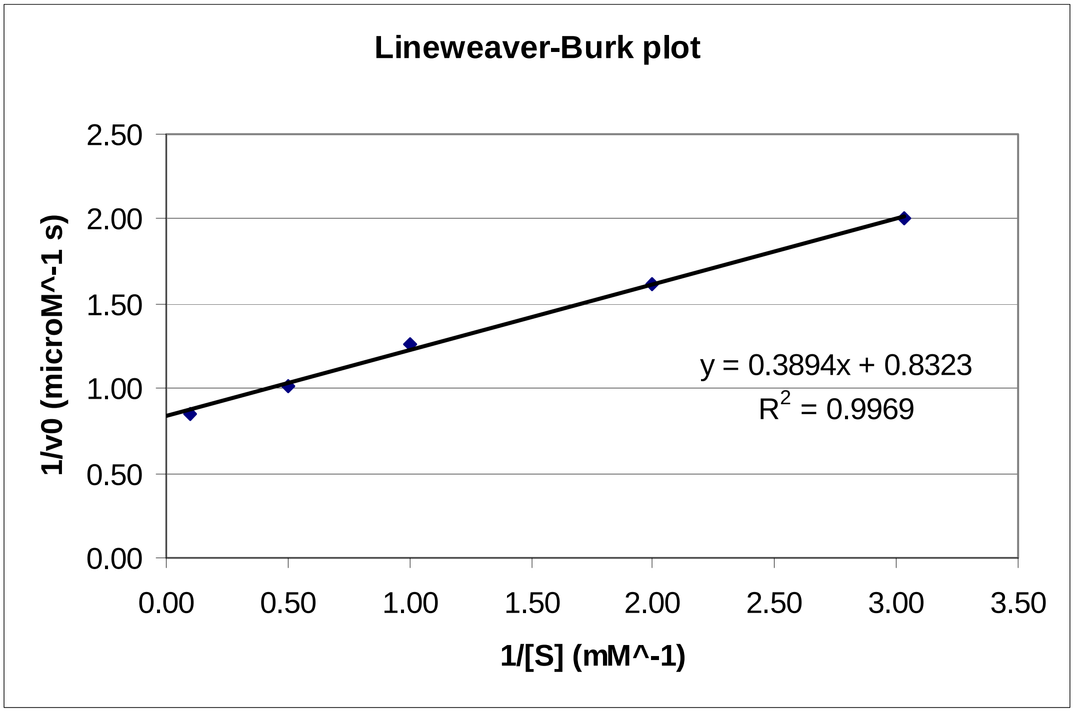
g) $k_1[E][O_2^-] = 2k_1[E^-][O_2^-]$, therefore $[E]/[E]_0 = 2$

h) $k = k_1 + k_2 = k_1 + 2k_1 = 3k_1$

$k_1 = 4.2 \times 10^8\ M^{-1}s^{-1}$ and $k_2 = 8.3 \times 10^8\ M^{-1}s^{-1}$

8.17 Sodium succinate (S) oxidized to form Sodium fumarate (F)

a) Lineweaver-Burk plot (again!)



b) $1/V_{max}$ is the y-intercept, or $0.8323\mu M^{-1}s$, therefore $V_{max} = 1.20 \times 10^{-6}M$
K_M/V_{max} = slope = 0.3894 $\rightarrow K_M = (\text{slope})V_{max} = (0.3894)(1.20 \times 10^{-3}M) = 4.68 \times 10^{-4}M$.

c) In the absence of inhibitor, $v_0 = V/(1 + K_M/[S]) = V(1+ 4.68\text{x}10^{-4}/1\text{x}10^{-3})=V/1.485$
In the presence of inhibitor, $v_0= V/(1 + K'_M/[S])$ where $K'_M = K(1 + [I]/K_I)$
$V/(2)(1.485) = V/(1 + K'_M/10^{-3})$
$K'_M = 10^{-3}(2.97 - 1) = 1.97 \times 10^{-3}M = (4.85 \times 10^{-4}M)(1 + 30\text{x}10^{-3}/K_I)$
$K_I = 30 \times 10^{-3}M/(4.06 - 1) = 9.8 \times 10^{-2}M$
Lineweaver-Burk plot with intercept $1/V = 0.815 \times 10^6 M^{-1}s$ and slope $K'_M/V = 1605s$.

8.29

a) for the three curves shown, $K'_M = K_M (1 + [I]/K_I) = (\text{slope})V = (\text{slope})/(9.3 \text{ min mM}^{-1})$

$[Nbs_2]$ (mM)	Slope (min)	K'_M (mM)	A plot of K'_M vs. $[Nbs_2]$ gives
0.25	31.3	3.36	Intercept = 2.4mM
0.50	40.4	4.34	Slope = 3.8
1.00	57.7	6.20	$V_R = 1.79\ \mu M\ s^{-1}$

b) $K^{eq} = V_F K^R_m / V_R K^F_m = (1.17\text{x}10^3)(5\text{x}10^{-7})(2.4\text{x}10^{-3})/(1.79\text{x}10^{-6})(5.7\text{x}10^{-5}) = 1.38\text{x}10^4$

that's all folks! Have a nice summer.